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The Structure of Diborane

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For over a decade numerous structural representations for diborane have been postulated.[1] Unfortunately, the large body of experimental data regarding this substance which accumulated during that period did not permit an unambiguous selection. Only within the past few years has it been realized that the existence of diborane may be accounted for without the introduction of *ad hoc* hypotheses; theoretical justifications based on the currently accepted theories of valence have been formulated[2] favoring the structure initially proposed by Sidgwick.[3] If the assumption relating interatomic distance in molecules with the corresponding "bond-type" be accepted,[4] a determination of the spatial arrangement of the atoms in diborane would lead to definite conclusions regarding its structure. Such a determination was undertaken and successfully carried through by means of an electron diffraction experiment on the vapor.

The Sample.—The diborane used in this investigation (32 cc. of the gas at S. T. P.) was prepared by Dr. Anton B. Burg at the University of Chicago according to the method devised in that laboratory,[5] purified by fractional condensations, and sent to Pasadena by air mail. Since the thermal decomposition of diborane has an induction period of several days, very little decomposition could have taken place during the time of transit (*circa* twenty-six hours) during which the sample was at room temperature. This was substantiated by the fact that no non-condensable material was found on opening the tube. Had some decomposition taken place among the resulting products there would have been hydrogen (the others—B_4H_{10}, B_5H_{11}, B_5H_9, $B_{10}H_{14}$, and non-volatile solids). The container was placed in liquid air immediately upon arrival and kept at that temperature except during the runs which lasted about twenty minutes during which the gas was permitted to warm up to temperatures in the neighborhood of −72°. All manipulations were carried out according to standard borane technique.

The Photographs.—Using electrons of λ 0.0613 Å., twelve photographs of varying density were obtained showing five to seven rings. The general qualitative features are sketched in Fig. 1. The similarity of the pattern produced by diborane to the one produced by ethane should be noted. Except for a change in the *s*-scale (due to the larger dimensions of the borane molecule its entire pattern is compressed) the two are identical; both have a faint inner peak followed by a shallow minimum and two poorly resolved intense maxima, the last appearing more like a shelf. The next minimum is deep; the fourth peak is of medium intensity and has a shoulder on the further side; there then follow several troughs and peaks in decreasing intensity somewhat regularly spaced. The contrast with the features presented by the ethylene photographs is apparent.[6]

Analysis.—The visually determined values of s [= $(4\pi \sin \theta/2)/\lambda$] for the apparent maxima and minima are given in Table I. These are the averages of measurements made by three observers. In the last column the ratios of the corresponding *s*-values for ethane and diborane are given. Since the measurements on the two sets

TABLE I

Max.	Min.	I	Wt.	$s_{\text{obsd.}}$	s_{model} B_1	B–B	B–H	$\frac{s_{C_2H_6}}{s_{B_2H_6}}$
2		17	24	5.44	5.89	1.906	1.300	1.13
	3		24	6.53	6.90	1.860	1.268	1.15
3		15	24	7.59	7.82	1.813	1.236	1.19
	4		48	9.13	9.48	1.827	1.246	1.18
4		10	48	10.62	11.32	1.876	1.279	1.18
4a		6	(20)	11.87				
	5		37	13.46	14.53	1.899	1.295	
5		5	37	14.93	16.15	1.904	1.298	1.17
	6		11	16.67	17.33	1.830	1.248	
6		2	17	18.14	18.38	1.783	1.216	1.18
7		1	(4)	21.82				
Weighted mean						1.862	1.270	
Weighted mean dev.						0.031	0.023	
When curve B_2 is used:								
Weighted mean						1.859	1.268	
Weighted mean dev.						0.036	0.025	
When curve D is used:								
Weighted mean						1.852	1.283	
Weighted mean dev.						0.030	0.021	

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(1) For a review of the present status of the problem see Egon Wiberg, *Ber.*, **69**, 2816 (1936). An extensive key to the literature is given.

(2) L. Pauling, THIS JOURNAL, **53**, 3225 (1931); R. S. Mulliken, *J. Chem. Phys.*, **3**, 635 (1935).

(3) N. V. Sidgwick, "The Electronic Theory of Valence," Oxford University Press, London, 1929, p. 103.

(4) Although this criterion has never been stated explicitly, it forms the basis upon which the structural interpretations made by L. Pauling and his collaborators rest, and is implied in the numerous publications by this school which have appeared in recent years. Experimental justification may be found in the *general* constancy of covalent radii except where theoretical deductions lead one to expect discrepancies. Compare, for instance: L. Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932); L. Pauling, L. O. Brockway, and J. Y. Beach, THIS JOURNAL, **57**, 2705 (1935).

(5) H. I. Schlesinger and A. B. Burg, *ibid.*, **53**, 4321 (1931).

(6) Unpublished data on the hydrocarbons were placed at the disposal of the author by Professor L. Pauling, to whom sincere thanks are expressed.

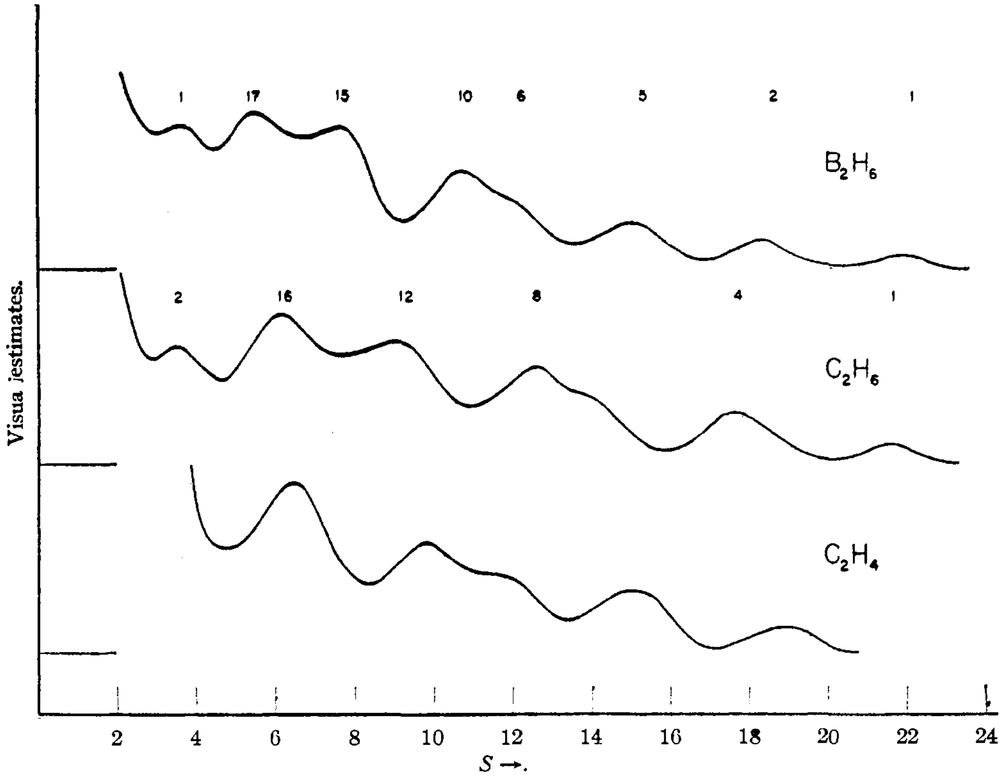

Fig. 1.—Curves representing visual appearance of electron diffraction photographs.

were made by different observers, one would not expect the inner rings to give reliable ratios due to the varying St. John effect. As s gets larger, this ratio assumes the essentially constant value 1.18. An estimate for the B–B separation can thus be made immediately. If the C–C distance in ethane is taken to be 1.55 Å., the corresponding distance in diborane would be roughly 1.55 × 1.18 = 1.83 Å. The above conclusions are in complete accord with the X-ray data on crystals of these two substances with regard both to the similarity of the structures and to the interatomic distances.[7]

Results of a six term radial distribution calculation using the tabulated intensities and s-values are plotted in Fig. 2. The prominent internuclear separations indicated are 1.32, 1.79, and 2.59. This is as good as may be expected from the application of the highly simplified procedure[8] to so light a molecule.

Theoretical intensity curves using the expression $I = \sum_{ij} Z_i Z_j \frac{\sin l_{ij} s}{l_{ij} s}$ were calculated for various

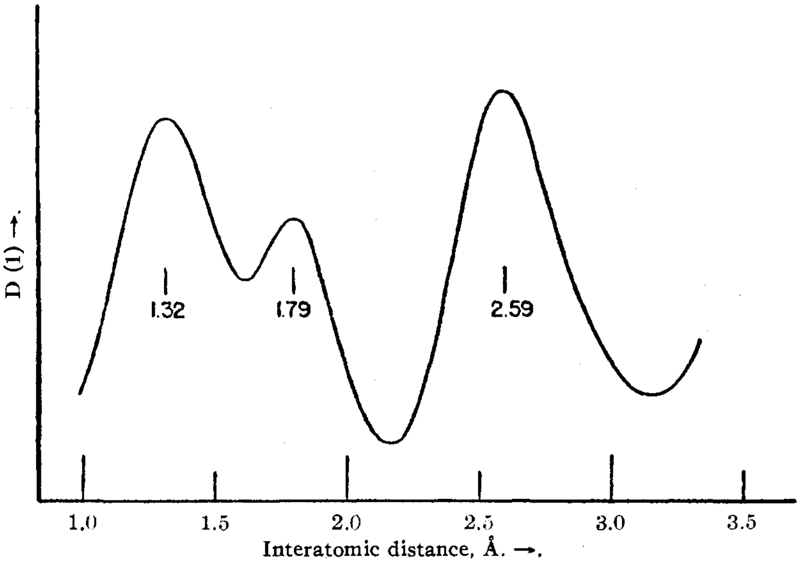

Fig. 2.—Radial distribution curve for diborane.

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(7) H. Mark and E. Pohland, *Z. Krist.*, **62**, 103 (1925).

(8) L. Pauling and L. O. Brockway, THIS JOURNAL, **57**, 2684 (1935).

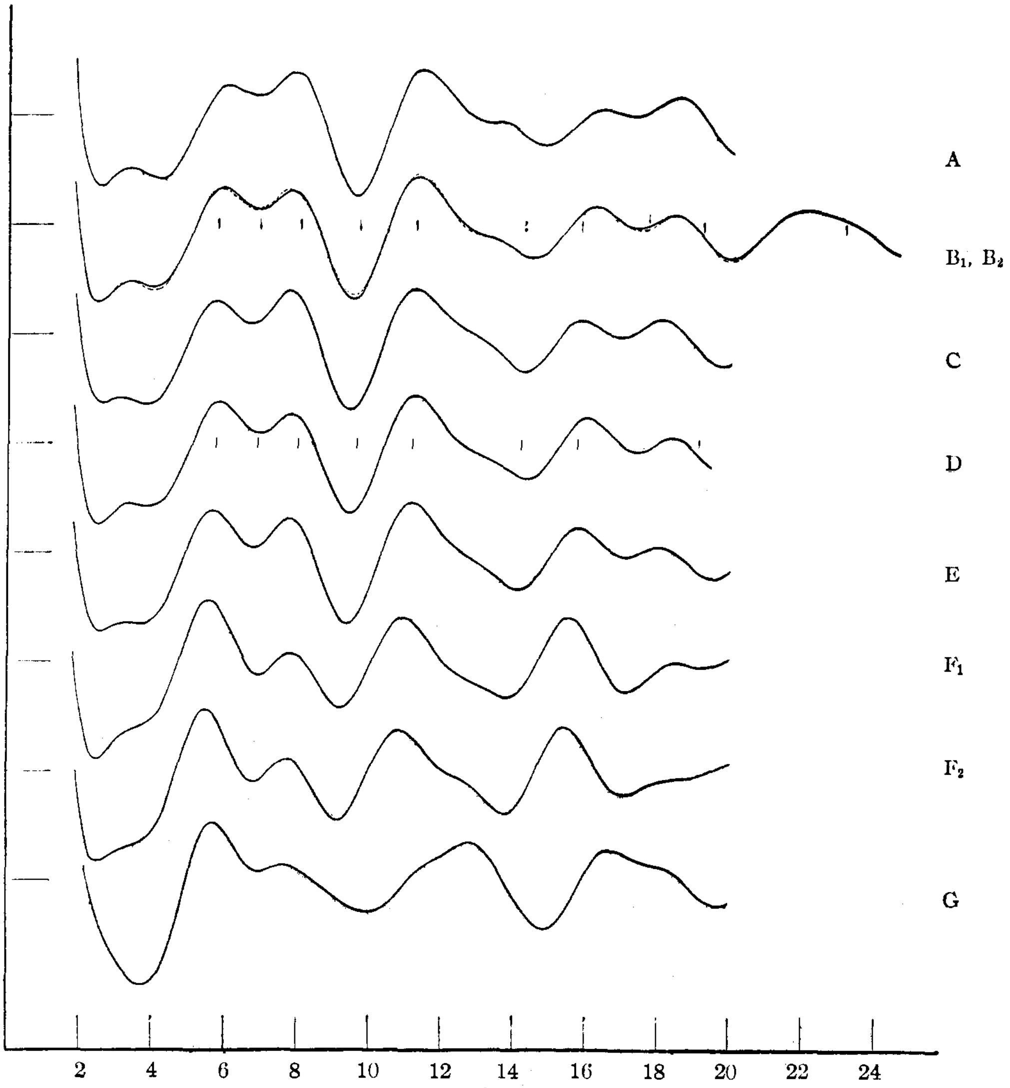

Fig. 3.—Calculated intensity curves. Arrows show best fit with measured ring diameters for models B and D, as obtained from Table I. Curve B_1 is full; B_2 is dashed.

models. Except where explicitly stated, the *cis* (sym. D_{3h}) and *trans* (sym. D_{3d}) orientations were given equal weight. Comparisons of curves B_1 and B_2 conclusively show that the effects on the pattern of free or hindered internal rotation are negligible.[9] In all the models the B–B distance was assumed to be 1.76 Å. except in model G, where it was taken to be 10% less. The curves are shown in Fig. 3.

Model A: Ratio (B–B/B–H) = 1.503 with all angles taken to be tetrahedral.

Eliminated, due to (1) improper intensity relationships between peaks 2 and 3, 5 and 6; (2) prominence of shoulder on the right side of peak 4.

Model B: Ratio = 1.466 with all angles tetrahedral.

For curve B_1 (full) equal weights were taken for the *cis* and *trans* forms.

For curve B_2 (dashed) only the *trans* position was considered.

This model was accepted as the one which gives the best qualitative and quantitative agreement with the experimental data.

Model C: Ratio—the same as for B. The B–B–H angles were assumed to be 113°.

Eliminated, due to (1) improper intensity relationships between peaks 2 and 3; (2) the particularly large quantitative discrepancies at the outer rings.

Model D: Ratio = 1.442 with all angles tetrahedral.

Although this model reproduces very well most of the qualitative features of the observed diffraction pattern, the

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[9] For ethane, experimental evidence is available that a potential barrier of the order of 2000–3000 calories restricts freedom of rotation of the methyl groups. See J. D. Kemp and K. S. Pitzer, THIS JOURNAL, **59**, 276 (1937); J. B. Howard, *Phys. Rev.*, **51**, 53 (1937).

shoulder on the right of peak 4 is too faint. The differences between the final interatomic distances as derived from this model and those obtained from B_1 are of the order of 0.01 Å. (Table I) and hence are well within the experimental error.

Model E: Ratio = 1.431, with the B–B–H angles assumed to be 113°.

Eliminated, due to very poor quantitative agreement at large s values.

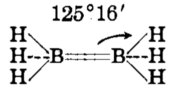
Model F: Ratio = 1.353.

For curve F_1 all angles were assumed to be tetrahedral.

For curve F_2 the B–B–H angles were assumed to be 112°.

Eliminated, due to distinct lack of qualitative and quantitative agreement with data. Model F_2 is the one obtained by taking the distances indicated by the radial distribution curve to correspond to B–H (bonded), B–B, and B–H (non-bonded), respectively.

Model G: Ratio = 1.352. An ethylene-like arrangement with two extra protons.

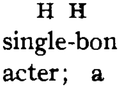


Eliminated, due to the obvious lack of correspondence with the data.

I found it difficult to construct a spatial model which would correspond unambiguously to the structure proposed by Wiberg.[1] If the distribution of H nuclei is the same as in ethane but with two boron atoms connected by a double bond, the ratio (B–B/B–H) would equal 1.351, *i. e.*, essentially model F_1 which may be eliminated as indicated. If the hydrogen atoms are distributed as shown in model G, the Wiberg structure may be equally well discarded. Indeed, it appears impossible to formulate a model having the two boron atoms doubly bonded which would result in a molecule large enough to produce diffraction rings of the observed diameters. Unfortunately the rings are not sufficiently sharp to warrant treating the data by means of the analytic method.[10]

Comparison of the various theoretical intensity curves with the one observed (Fig. 1) eliminates models A, C, E, F, and G. D has the defect of not indicating a sufficiently prominent shoulder on peak 4, whereas B reproduces well all the qualitative features of the observed pattern and is in good quantitative agreement with the data (Table I). This model corresponds to an ethane-like structure with the ratio of (B–B/B–H) equal to 1.466. From the values of $s_{\text{obsd.}}$ and $s_{\text{calcd.}}$ the following conclusions regarding the dimensions of diborane are deduced: (a) The atoms are arranged in the form of two pyramids (axes coincident), their apices, at which the boron atoms are located, pointing toward each other. (b) The B–B distance is 1.86 ± 0.04 Å.; the B–H distance is 1.27 ± 0.03 Å. (The probable errors indicated were taken somewhat larger than the weighted mean deviation as calculated in Table I.) (c) The valence angles of the boron atoms are tetrahedral to within three degrees. The correspondence of these results with the ones obtained through the comparison of the patterns of ethane and diborane should be noted.

Discussion.—The nuclear configuration found for diborane by the electron diffraction method can be immediately interpreted in terms of the nature of the bonds in the molecule. This is done below; a further more detailed description of the electronic structure of the molecule from the valence-bond and the molecular-orbital points of view is also given, followed by a discussion of the chemical and physical properties of the substance.

The tetrahedral radius for a boron atom with a completed octet has been assigned the value 0.89 Å.,[11] from extrapolation of the sequence F, O, N, C; this value is also indicated by the comparison of BH with CH and other diatomic hydrides. We accordingly would expect for the B–B and B–H single bond distances 1.78 and 1.18 Å., respectively. In the two cases which have been studied experimentally the boron atoms did not possess completed octets, yet dimensions of this order or somewhat smaller were observed; thus the B–B distance in CaB_6 is 1.716 Å.,[12] and in B_5H_9 an average value of 1.76 Å. is obtained.[13] In the molecule BH the B–H separation is found to be 1.226 Å. While it is generally true that in the diatomic hydrides the internuclear distance is greater than in the corresponding polyatomic hydride molecules (C–H = 1.09 in CH_4, 1.12 in CH), in diborane the situation is reversed. *Actually, the values for the B–B and B–H distances in B_2H_6 are both considerably larger than the single-bond separations, showing that all the bonds in the molecule have to some extent the character of bonds weaker than "single" bonds.* This is expected for the B–H bonds on the basis of Sidgwick's structure  $\mathrm{H}\cdot\overset{\mathrm{H}}{\underset{\ddot{\mathrm{H}}}{\ddot{\mathrm{B}}}}:\overset{\mathrm{H}}{\underset{\ddot{\mathrm{H}}}{\ddot{\mathrm{B}}}}\cdot\mathrm{H}$, which gives each B–H two-thirds single-bond and one-third one-electron-bond character; a slight extension of this configuration considering resonance to structures such as

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(10) S. H. Bauer, *J. Chem. Phys.*, **4**, 406 (1936).

(11) L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).

(12) L. Pauling and S. Weinbaum, *ibid.*, **A87**, 181 (1934).

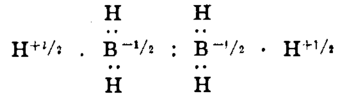
(13) S. H. Bauer and L. Pauling, THIS JOURNAL, **58**, 2403 (1936).

$\mathrm{H}\cdot\underset{\ddot{\mathrm{H}}}{\overset{\mathrm{H}}{\ddot{\mathrm{B}}}}\cdot\underset{\ddot{\mathrm{H}}}{\overset{\mathrm{H}}{\ddot{\mathrm{B}}}}:\mathrm{H}$ also would further account for the observed increase of the B–B bond distance. The observed distances are equally compatible with Lewis' structure, representing resonance among the seven arrangements $\mathrm{H}:\underset{\ddot{\mathrm{H}}}{\overset{\mathrm{H}}{\ddot{\mathrm{B}}}}\ \ \underset{\ddot{\mathrm{H}}}{\overset{\mathrm{H}}{\ddot{\mathrm{B}}}}:\mathrm{H}$, $\mathrm{H}\,\underset{\ddot{\mathrm{H}}}{\overset{\mathrm{H}}{\ddot{\mathrm{B}}}}:\underset{\ddot{\mathrm{H}}}{\overset{\mathrm{H}}{\ddot{\mathrm{B}}}}:\mathrm{H}$, etc., and giving each bond $^6/_7$ single-bond character and $^1/_7$ no-bond character. However, strong theoretical arguments may be given to support the view that *the molecule resonates among all the structures of the Sidgwick and Lewis types*, the B–B and the B–H bonds having single-bond, one-electron-bond, and no-bond character.

It is especially significant that shortening the B–B distance below the single-bond value, as would be required for any structure giving the B–B bond some double-bond character, is not observed. This eliminates all structures such as Wiberg's.

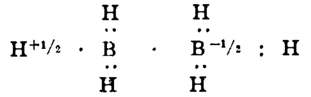
In the language of atomic orbitals the structure of diborane should therefore be described as follows: The allowed orbitals for boron are four in number, of the hybridized sp^3 type, directed toward the corners of a tetrahedron. Each of these may be occupied by a shared electron-pair, by a single electron, or left empty. Thus the valence-bond configurations which contribute to the ground state are (formal charges indicated):

I



$$\mathrm{H}^{+1/2}\ .\ \underset{\mathrm{H}}{\overset{\mathrm{H}}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{B}}}}}{}^{-1/2}\ :\ \underset{\mathrm{H}}{\overset{\mathrm{H}}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{B}}}}}{}^{-1/2}\ \cdot\ \mathrm{H}^{+1/2} \qquad (9)$$

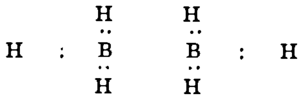
II



$$\mathrm{H}^{+1/2}\ \cdot\ \underset{\mathrm{H}}{\overset{\mathrm{H}}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{B}}}}}\ \cdot\ \underset{\mathrm{H}}{\overset{\mathrm{H}}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{B}}}}}{}^{-1/2}\ :\ \mathrm{H} \qquad (6)$$

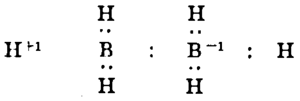
[14]

III



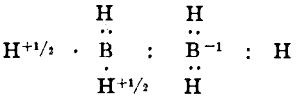
$$\mathrm{H}\ :\ \underset{\mathrm{H}}{\overset{\mathrm{H}}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{B}}}}}\qquad \underset{\mathrm{H}}{\overset{\mathrm{H}}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{B}}}}}\ :\ \mathrm{H}$$

IV



$$\mathrm{H}^{+1}\quad \underset{\mathrm{H}}{\overset{\mathrm{H}}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{B}}}}}\ :\ \underset{\mathrm{H}}{\overset{\mathrm{H}}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{B}}}}}{}^{-1}\ :\ \mathrm{H} \qquad (6)$$

V



$$\mathrm{H}^{+1/2}\ \cdot\ \underset{\mathrm{H}^{+1/2}}{\overset{\mathrm{H}}{\underset{\cdot}{\overset{\cdot\cdot}{\mathrm{B}}}}}\ :\ \underset{\mathrm{H}}{\overset{\mathrm{H}}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{B}}}}}{}^{-1}\ :\ \mathrm{H} \qquad (6)$$

so that the wave function of diborane may be represented approximately by a linear combination of the wave functions of the above structures. The question as to their relative weights will be discussed later; nevertheless, it is evident that the contributions of the structures II and III will tend to weaken the B–B bond. Combination of II and IV alone gives the arrangement proposed by G. N. Lewis.[15] His description requires that all the electrons remain paired but not that they occupy all the orbitals simultaneously. Through this argument he was led to predict the diamagnetism and characteristic weak bonds of diborane.

Although the individual members of the structural types II, IV, and V do not have the symmetry which we associated with diborane (D_{3d}),

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[14] Justification for writing structures of type 1, that is, configurations involving a one-electron bond between B_2H_5 and H, has already been presented [L. Pauling, THIS JOURNAL, **53**, 3225 (1931)]. Professor Pauling then estimated that the coulomb attraction, at small distances, of $B_2H_5^-$ and H^+ may contribute as much as 10 or 11 volts to the energy of the aggregate. In order to justify structures of type II wherein a one-electron-bond is placed between the two BH_3 groups one must show that the systems (a) $BH_3^+ + BH_3^-$ (when in valence state), and (b) $BH_3 + BH_3$ (when in valence state) have energies which are nearly equal at small internuclear separations. The following rough estimates indicate that this is the case.

In (a): The ionization potential of a BH_3 radical when in its ground state ($[sa_1]^2\ [\pi e]^4$, $^1A_1$) may be taken equal to 12.6 volts. This value was suggested by Prof. Mulliken on the ground that the energy of removal of a $[\pi]$ electron (B–H bonding) should be approximately the same when in a free BH_3 group as when in B_2H_6. The configuration of the ion is $[sa_1]^2\ [\pi e]^3$. On the other hand, the electron affinity of a BH_3 radical (closed shell structure) must be rather close to zero; the capture of an electron leads to the ion BH_3^-, $[sa_1]^2\ [\pi e]^4\ [\sigma a_1]$. If the contribution of the coulomb energy of the two ions at small separations is taken to be ten volts, as in the case of $B_2H_5^-$ and H^+, the energy of the resulting aggregate is in the neighborhood of 2–3 volts above that of two BH_3 ($^1A_1$) groups. On very close approach these will combine to form the molecule B_2H_6, $[sa_1]^2\ [sa_1]^2\ [\pi e]^4\ [\pi e]^4\ [\sigma + \sigma, a_{1g}]$, $^{1,3}E_g$, etc. If a $^1A_1$ state is desired for the final diborane the process which must be followed is described schematically

$$\left.\begin{array}{l} BH_3(^1A_1) \xrightarrow{12.6\text{v}} BH_3^+,\ ([sa_1]^2\ [\pi e]^3 \xrightarrow{4\text{v}} \\ \qquad\qquad\qquad\qquad (BH_3^+)^*,\ ([sa_1]\ [\pi e]^4) \\ BH_3(^1A_1) \xrightarrow{0\text{v}} BH_3^-,\ ([sa_1]^2\ [\pi e]^4\ [\sigma a_1]) \end{array}\right\} \xrightarrow{-10\text{v}}$$

$$\underbrace{(BH_3^+)^* + BH_3^-}_{\text{is approximately seven volts above two } BH_3\ (^1A_1) \text{ groups.}} \longrightarrow (B_2H_6)^*,\ [sa_1]\ [sa_1]^2\ [\pi e]^4\ [\pi e]^4\ [\sigma + \sigma, a_{1g}],\ ^1A_{1g}, \text{ etc.}$$

In (b): Since the combination of two BH_3 radicals results in repulsive states only, it is necessary to excite one of them to the configuration $(BH_3)''$, $[sa_1]^2\ [\pi e]^3\ [\sigma a_1]$. This process requires an energy equivalent to 2–3 volts. Hence the resulting aggregate is near in energy to that obtained above from the close approach of the unexcited ions, *i. e.*, leading to B_2H_6, $^{1,3}E_g$, etc. Again, if a $^1A_1$ state is desired for the diborane molecule, the corresponding schematic process is

$$\left.\begin{array}{l} BH_3(^1A_1) \xrightarrow{2\text{–}3\text{v}} (BH_3)'',\ ([sa_1]^2\ [\pi e]^3\ [\sigma a]) \xrightarrow{4\text{v}} \\ \qquad\qquad\qquad\qquad (BH_3)''^*,\ ([sa_1]\ [\pi e]^4\ [\sigma a]) \\ BH_3(^1A_1) \end{array}\right\} \xrightarrow{0\text{v}}$$

$$\underbrace{(BH_3)''^* + BH_3}_{\text{is approximately 6–7 above two unexcited } BH_3 \text{ groups.}} \longrightarrow (B_2H_6)^*,\ ^1A_{1g}, \text{ etc.}$$

[15] G. N. Lewis, *J. Chem. Phys.*, 1, 17 (1933).

symmetric and antisymmetric linear combinations of the six components of each type will result in two configurations of equal energy, one of which (the symmetric) may be used in further combinations with I and III. The latter interaction will cause the energy of the over-all symmetric combination to be lowered and of the remaining antisymmetric one to be raised, so that the ground state of diborane will be of the A_1 type. Let us now attempt to deduce its multiplicity. Structures III and IV are in singlet states; I, II, and V may have the spins of the electrons participating in the one-electron-bonds either parallel or antiparallel, but only when in the latter arrangement are the structures permitted to combine with III and IV.[16] The relative energies of the singlet and triplet states of the structures belonging to the Sidgwick configuration will vary with the different types, but this we cannot estimate in the present treatment. However, since the interaction of the structures having resultant spin zero with the ones belonging to the Lewis configuration will give a state whose energy is lower than that of either configuration alone, we may conclude that the ground state will be singlet, *i. e.*, that diborane has a ground state ($^1A_1$) which is diamagnetic, as observed, and a low-lying paramagnetic state ($^3A_2$) whose existence has not yet been verified.

Professor Mulliken has already given a molecular orbital treatment of this and related molecules.[2] The present data make possible unambiguous decisions for several questions arising in that discussion, the answers for which heretofore could be only surmised. Very roughly, the following configurations may be correlated with the various structures listed above[17] (omitting the 1s electrons of boron):

IM $[s + s, a_{1g}]^2\ [s - s, a_{2u}]^2\ [\sigma + \sigma, a_{1g}]^2\ [\pi e]^3\ [\pi e]^3$, $^1A_{1g}$, etc. with I

IIM $[s + s, a_{1g}]\ [s - s, a_{2u}]^2\ [\sigma + \sigma, a_{1g}]\ [\pi e]^4\ [\pi e]^4$, ^1A_1g, etc. with II

IIIM $[sa_1]^2\ [sa_1]^2\ [\pi e]^4\ [\pi e]^4$, $^1A_{1g}$ with III

IVM $[s + s, a_{1g}]^2\ [s - s, a_{2u}]^2\ [\sigma + \sigma, a_{1g}]^2\ [\pi e]^4\ [\pi \theta]^2$, $^{1,1}A_{1g}$, etc. with IV + V

where the $[\sigma + \sigma]$ electrons are mainly B–B bonding and the others are essentially confined to the B–H bonds (the $[s + s]$ electrons also contribute to the B–B bond).

It will be noted that whole-molecule orbitals were written for the $[sa_1]$ electrons in IM, IIM, and IVM, whereas this was not done for the $[\pi e]$ electrons. The reason is evident. Since the former are nearly but not entirely confined to the BH_3 groups, while the $[\sigma + \sigma]$ electrons, although strongly B–B bonding, also assist in the B–H bonds, their wave functions overlap, so that a hydridization (between the $[s + s]$ and $[\sigma + \sigma]$) which becomes possible only after the linear combination of the $[sa_1]$ orbitals is made, would result in a somewhat better representation of the electron configuration. As in ethane, this interaction will cause the $[\sigma + \sigma]$ electrons to have a somewhat lower ionization potential and the $[s + s]$ electrons a correspondingly higher one. Similarly, the use of whole-molecule orbitals $[\pi + \pi, e_u]$, $[\pi - \pi, e_g]$ would indicate a resonance between the $[\pi e]$ electrons of the two BH_3 groups. This would necessitate that the $[\pi]$ bonding be very strong, and that there be considerable overlapping of their wave functions in the region between the boron atoms, introducing effectively a double bond contribution. Each of the BH_3 groups would then have a tendency to be planar. The observed spatial structure is distinctly contrary to such an hypothesis. The B–H as well as the B–B distances are larger than might have been expected even for pure single bonds, and the BH_3 groups are pyramidal. Indeed this state of affairs was anticipated by Mulliken on the basis of the fact that diborane does not have an absorption region in the visible. Hence,[2] his configurations 1a, 2a, and 3a are definitely eliminated. In IIIM the $[sa_1]$ electrons were placed in the radical orbitals since this arrangement corresponds to repulsion between the BH_3 groups.

The question arises whether all the states listed have sufficiently low energies to contribute appreciably to the ground state. By correlating, respectively, the IM and IIIM configurations with the two $^1A_1$ ($[sa_1]^2\ [\pi e]^4$) and two ^3E ($[sa_1]^2\ [\pi e]^3\ [\sigma a_1]$) states of the separated BH_3 groups, Mulliken was able to estimate that the unperturbed levels corresponding to the $^1A_{1g}$ states of IM and IIIM would be approximately one volt apart and that the interaction energy would be of the order of one-half volt. The energy of con-

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[16] For the resonance criteria among several structures see L. Pauling, THIS JOURNAL, **54**, 988 (1932).

[17] For the present, configurations giving rise to $^1A_1$ states will be considered since only these are permitted to interact with the structures which appear to give the largest contribution to the ground state (I and III). The correlations indicated to the right refer to the symmetric linear combinations of the individual members of the particular type.

figuration IVM is probably slightly above that of IM since in going from the latter to the former an electron is merely transferred from a [π] orbital of one BH_3 group to the same orbital in the other. State IIM, however, is highly excited. The corresponding unexcited one is given by Mulliken

IIM $[s + s, a_{1g}]^2\ [s - s, a_{2u}]^2\ [\sigma + \sigma, a_{1g}]\ [\pi e]^4\ [\pi e]^3$, $^{1,3}E_g$, etc.

Since the ionization potential of the [s] electrons was estimated at approximately 17 volts while that of the [π] electrons only 12.6 volts and of the [$\sigma + \sigma$] at 13.0 volts,[2,18] IIM lies far above IIm. The latter cannot interact with IM, IIIM, and IVM while the former may but can contribute only slightly to the ground state due to the fact that it is so far removed from the other components. Hence, when diborane is in its lowest energy state, its structure may best be represented by a combination of the configurations IM, IIIM, and IVM with very little of IIM. (IIIM must make an appreciable contribution in order that the large B–B separation may be accounted for.) Let us now return to the atomic orbital treatment and specify that the magnitudes of the coefficients in the linear combination for the wave function of diborane are probably in the order: I, III, IV, and V with very little of II (excited).

The compounds B_4H_{10} and B_5H_{11} which presumably have chain-like structures should have electron configurations, and B–B and B–H distances entirely analogous to those found in diborane, as contrasted with the ring structure of B_5H_9.[13]

Discussion of the Physical Properties.—Four physical constants of diborane have been measured. These are quoted by Wiberg[1] in support of his structure. Let us see how they may be interpreted in terms of the structure given by the electron diffraction study.

(1) **Diamagnetism.**—The ground state of the configuration discussed above is of the singlet symmetric type and hence is diamagnetic.

(2) **Lack of Electric Dipole Moment.**—Both Profs. Pauling and Mulliken stressed the fact that in their formulation (as in the amplified one presented in this paper) all the hydrogen atoms are equivalent. Diborane consequently should have no moment.

(3) **Similarity of Ultraviolet Absorption Spectrum to that of Ethylene.**—The deduction that in diborane the boron atoms are doubly bonded from the similarity of its ultraviolet absorption spectrum to that of ethylene is fallacious. An explanation of the two continuous regions of absorption on the basis of Mulliken's electron configuration (which is essentially the one given in this analysis) has been suggested by E. Blum and G. Herzberg.[19]

Professor Mulliken reports [*J. Phys. Chem.*, February, 1937] that diborane shows no absorption in the near ultraviolet, visible, and photographic infrared ($\lambda 2500$–$\lambda 12{,}000$). This is somewhat puzzling since various low-lying electronic levels to which transitions from the ground state are not forbidden have been predicted.[2]

(4) **Parachor.**—Stock and collaborators made a careful determination[20] of the surface tension and density of diborane. As far as the author is aware, this is the first investigation of its kind which has been carried out on a compound the structure of which must be represented by one-electron-bonds resonating with electron-pair-bonds. Since the contribution to the parachor of any type of bond can only be determined experimentally, one cannot draw any conclusions regarding the structure of this compound from the value of its surface tension. Deductions made from phosphorus and arsenic pentachlorides (which gave the value −12.4, employed by Wiberg, in obtaining the parachor of the Sidgwick structure) are entirely without foundation since most chemists believe that the latter molecules have no "singlet" bonds. However, the work of Stock and collaborators would permit one to calculate an appropriate number which might be used in future structure determinations.

Wiberg admits[1] that the available chemical evidence is in harmony with the Sidgwick configuration. The modifications introduced by Pauling, Mulliken and in the present discussion do not alter this state of affairs. Since the types of bonds found in diborane and its homologs are essentially unlike those in other molecules ordinarily dealt with by chemists one cannot safely reason by analogy. Predictions as to how such molecules behave chemically can be made only after sufficient empirical data have been gathered.

Resonance Energy of Diborane.—The heat of formation of diborane from solid boron and molecular hydrogen was recently determined to

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(18) A similar inequality amounting approximately to eight volts is given for ethane; R. S. Mulliken, *J. Chem. Phys.*, **3**, 517 (1935).

(19) E. Blum and G. Herzberg, *J. Phys. Chem.*, **41**, 91 (1937)

(20) A. Stock, E. Wiberg and W. Mathing, *Ber.*, **69**, 2811 (1936).

be 44 ± 3 kcal.[21] We are now in a position to make an estimate of the resonance energy in diborane. Let us first consider the reaction $B(s) + 1^1/_2H_2 = BH_3(g)$. Since the electronegativities of boron and hydrogen are identical for purposes of calculation there are no heat effects due to the ionic contributions of the bonds. Hence if the solid consists of boron atoms which are bonded to three others by single bonds it is clear from Pauling's additivity rule that the above reaction will be accompanied by a zero heat effect since for every B–H bond which is formed one-half an H–H and one-half a B–B bond will be broken. On the other hand, it appears quite likely that in the solid the boron atoms are tetrahedrally bonded, thus making use of all the orbitals available to them by means of some resonance scheme; then more bonds will be broken in the vaporization process than will be formed in the hydrogenation. Consequently the reaction giving rise to BH_3 radicals will be endothermic by an amount equivalent to the resonance energy present in solid boron. But the heat of formation of diborane from the elements was found to be exothermic. Hence we must conclude that the reaction $2BH_3 = B_2H_6$ is exothermic to the extent of 44 kcal. if the first alternative is assumed or to the extent of 44 kcal. plus the resonance energy available for each pair of atoms in solid boron if the second is preferred.

The stability of B_2H_6 relative to BH_3 or B_2H_4 is due to the resonance energy made possible in the former compound by the complete use of all the four orbitals permitted to boron atoms. From the arguments presented in the preceding paragraph we may estimate that a minimal value for this energy is 44 kcal. and may be set equal to the latter figure plus the resonance energy for a pair of boron atoms in the solid element.

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Summary

Electron diffraction photographs of diborane indicate that this compound has an ethane-like structure with the B–B distance equal to 1.86 ± 0.04 Å. and the B–H distance 1.27 ± 0.03 Å.; the valence angles of the boron atoms are found to be tetrahedral within three degrees. An electron configuration compatible with the large interatomic distances is presented both in terms of the atomic and molecular orbital modes of description and the conclusion is reached that the stability of B_2H_6 relative to BH_3 is due to the resonance energy made available through the full use of the four orbitals of boron.

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[21] W. A. Roth and E. Börger, *Ber.*, **70**, 48 (1937).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Activation of Specific Bonds in Complex Molecules at Catalytic Surfaces. III. The Carbon–Hydrogen and Carbon–Carbon Bonds in Propane and Ethylene

BY KIYOSHI MORIKAWA,[1] N. R. TRENNER[2] AND HUGH S. TAYLOR

The present research represents an extension to propane and ethylene of investigations previously reported by Morikawa, Benedict and Taylor dealing with methane[3] and ethane.[4] In the latter communication attention was directed to an abnormally high inhibitory action of hydrogen on the surface hydrogenation decomposition of ethane to yield methane. We have examined in the present work, in a more detailed manner, the kinetic relations of the decomposition and exchange reactions between propane and deuterium with results which confirm and extend our observations with ethane. Isotope exchange reactions with ethylene are also included as well as other supporting studies leading to a general discussion of the whole problem of activation in such hydrocarbon systems.

Experimental Details

Materials.—In addition to those gases described in the previous papers,[3,4] we have employed propane, ethylene

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[3] Morikawa, Benedict and Taylor, THIS JOURNAL, **58**, 1445 (1936).

[4] Morikawa, Benedict and Taylor, *ibid.*, **58**, 1795 (1936).